

Search for Selective Ion Diffusion Through Membranes

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SEARCH FOR SELECTIVE ION DIFFUSION THROUGH MEMBRANES

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SUMMARY

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In this study, we measured the diffusion rates of several ions through some membranes developed as battery separators at Lewis Research Center. The ions investigated were Li^+ , Rb^+ , Mg^{++} , Cl^- , and $\text{SO}_4^{=}$. The membranes were cross-linked polyvinyl alcohol, cross-linked polyacrylic acid, a copolymer of the two, cross-linked calcium polyacrylate, cellulose, and several microporous polyphenylene oxide-based films. No true specificity for diffusion of any of these ions was found for any of the membranes. But the calcium polyacrylate membrane was found to exhibit ion exchange with the diffusing ions giving rise to the leaching of the calcium ion and low reproducibility. These findings contrast earlier work where the calcium polyacrylate membrane did show specificity to the diffusion of the copper ion.

In general, Fick's law appeared to be obeyed. Except for the microporous membranes, the coefficients for ion diffusion through the membranes were comparable with their values in water. For the microporous membranes, the values found for the coefficients were much less, due to the tortuosity of the micropores.

INTRODUCTION

Recently, several new in situ cross-linking techniques have been developed for polyvinyl alcohol (PVA) and polyacrylic acid (PAA) films (refs. 1 to 3). Cross-linking converts these otherwise water soluble films into insoluble ones. These films were developed for use as separators in alkaline secondary batteries because data (ref. 3) indicate that the zincate ion diffusion coefficient through a cross-linked PVA film in alkaline electrolyte is low. Other data (ref. 4) show that the calcium salt of cross-linked PAA has ion exchange capabilities; the calcium ion readily exchanges with metal cations such as those of silver, copper, and cobalt. More recent work (ref. 5) has better defined the ion exchange reaction between the aqueous copper ion and the cross-linked calcium polyacrylate membrane: a phase of copper polyacrylate builds up as a layer on the surface of the membrane and this inhibits the diffusion process. These findings indicate that such membranes could be used to remove metal ions from solution and may afford certain advantages, namely, convenience of handling, over granular ion exchange resins.

To assess further the potential utility of these hydrophilic membranes, this study was made to determine whether any of these membranes exhibited ion selectivity for the diffusion of the simple ions: lithium (Li^+), rubidium (Rb^+), magnesium (Mg^{++}), chloride (Cl^-), and sulfate ($\text{SO}_4^{=}$). Our approach was to determine the relative diffusion rates of these ions through these cross-linked membranes as well as through cellulose and some microporous composite films. The data are reported in terms of D , the diffusion coefficient, and the ratio of D 's for a particular membrane. None of the ion selectivities varied any more than 30 percent from the selectivity of the respective ion in water; such a variation is deemed insignificant.

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EXPERIMENTAL

Background. - The determination of the true diffusion coefficient of an ion cannot be made directly with a single measurement because any ion must be accompanied by an ion of the opposite charge to preserve neutrality. The coefficient from a single measurement is a complex function of those of the cation and anion involved (refs. 6 and 7); the apparent coefficient is influenced by the ionic environment. However, in our investigation to ascertain possible ion specificity in diffusion through several selected membranes, we avoided the complexity of different ionic environments by measuring the diffusion rate of two different ions in the same solution. For example, when the diffusion of two cations were to be compared, the starting solution was equimolar in the two cations with a common anion. To determine if ion specificity existed for a particular membrane, this ratio of the apparent diffusion coefficients was compared with the corresponding ratio for a hydrophobic microporous film which should have one equal to that for an aqueous solution.

Cell. - The diffusion cell used was a commercial dialysis cell made of polymethylmethacrylate (see fig. 1). The membrane under study divided the cell into two cylindrical chambers which we designate as the right (r) and left (l) compartments. Each compartment was 19.0 mm in diameter and about 4.8 mm in thickness. Liquid could be added to and withdrawn from each compartment separately through the holes shown by using a syringe with a Teflon tubing attached.

Procedure. - The diffusion experiments were performed at $23 \pm 1^\circ \text{C}$. The method used for determining diffusion coefficients through the membranes consisted of placing an aqueous salt solution containing the ions under study in compartment (l) and distilled water into compartment (r). The compartments were filled up to the bottom of the filling holes. The ions of the salts diffused through the membrane causing the concentrations of the salts in compartment (l) to decrease and the concentration in compartment (r) to increase. Convection in this type of cell is sufficient to keep the concentration in each compartment essentially uniform (ref. 8). Osmosis also occurred to some extent; but osmosis should not affect the measured ratio of the diffusion rates for two different ions. After equal increments of time (one half hour each) the solution in compartment (r) was removed and replaced with distilled water. The solutions from compartment (r) were analyzed quantitatively for the ions of interest. After four hours, the solution in compartment (l) was removed; this ended the run. The solution from compartment (l) was also analyzed quantitatively for the ions. The cations were determined by atomic absorption; the anions were analyzed by a chromatographic method. The values of the diffusion coefficients and their ratios were calculated from the equations given in the Appendix. The volume of each compartment needed for the calculations were determined by transferring the water from a filled compartment to a tared bottle and weighing.

Materials. - The three aqueous salt solutions used in this study were: (1) 0.5 molar in lithium chloride (LiCl) and 0.5 molar in rubidium chloride (RbCl), (2) 0.5 molar in lithium chloride and 0.5 molar in magnesium chloride (MgCl_2), and (3) 0.5 molar in sodium chloride (NaCl) and 0.5 molar in sodium sulfate (Na_2SO_4).

Most of the membranes tested were hydrophilic polymeric membranes. The membranes belonging to this group were: cross-linked PVA; cross-linked PAA; the a cross-linked PVA-PAA copolymer in a 2 to 1 ratio; and cellulose. Ionic diffusion through these membranes occurs by ions passing between molecules of the membrane polymer. Such membranes are termed molecular porous in contrast

to microporous hydrophobic membranes which have fixed pores or channels; these pores are considerably larger than the inter-molecular distances within the polymer. Ionic diffusion occurs through these latter membranes by means of narrow aqueous solution pathways that extend from one face of the membrane to the other. The microporous membranes tested were: polyphenylene oxide containing magnesium oxide (MgO-ppo), polyphenylene oxide containing magnesium silicate (MgSiO₃-ppo), and polyphenylene oxide with the filler leached out (ppo).

The cellulose membrane was a commercial product of 90 micrometer thickness and 28 nanometer pore size. All the other membranes were prepared at this laboratory. The PVA and the copolymer were made by using a radiation cross-linking technique described in reference 2; the starting material was commercial high molecular weight linear polymer. The PAA and CaPA were also made by radiation cross-linking as described in reference 4. The preparations of the MgO-ppo and MgSiO₃-ppo are given in reference 8. The ppo membranes without filler were prepared by leaching the MgO filler out of MgO-ppo membranes; each 2 by 2" film of MgO-ppo was treated with 3 sequential 100 ml portions of hot, 1 normal hydrochloric acid for one hour each. The film was then rinsed seven times with 100 ml portions of water. Analysis of the hydrochloric acid solutions indicated that all of the MgO was removed from the membrane.

RESULTS AND DISCUSSION

The diffusion coefficient ratios for the membranes investigated are given in table I together with the membrane thicknesses. The ratios given are the averages over time; the average reproducibility was ± 5 percent. The least reproducibility occurred in the chloride-to-sulfate ratios (footnote e) for the microporous membranes. This low reproducibility is attributed to the extremely small amount of chloride and sulfate in the diffusate due to their very low diffusion coefficients; refer to table II.

We attribute the somewhat larger scatter for the CaPA membrane (table I, footnote b) to the highly ionic character of the membrane which allowed rapid ion exchange. As various cations diffused through the membrane the diffusing ion would replace the calcium ion; this was confirmed by the presence of the calcium ion in the diffusate (table I, footnote b). This ion exchange in turn would cause a deviation from the Fick's law, systematic error in the diffusion coefficients, and a larger than usual scatter in the data. The same type of ion exchange should also occur in PAA, but the extent of exchange is expected to be less because PAA is only weakly ionic (PAA is a weak acid). The resultant smaller deviations from Fick's law are reflected in better reproducibility in the data.

For the MgO-ppo membrane, leaching of the magnesium ion was found experimentally. But this did not result in low reproducibility. The MgO was held in suspension only as a filler in the polymer matrix. Thus, during the diffusion measurement the MgO was merely dissolved out and no ion exchange occurred. This resulted in essentially no deviation from Fick's law and good reproducibility.

Selectivity. - The values of $D(\text{Rb}^+)/D(\text{Li}^+)$ in table I average about 1.7. This is in good agreement with the value for our "nonselective" porous membrane. Also, there is very little scatter between this ratio for the various membranes. The greatest deviation from the average is 15 percent, that for the MgO-ppo membrane. Moreover, our average agrees closely with the

value of 1.5 that we calculated from literature values for the diffusion of these ions in dilute aqueous solution (refs. 9 and 10). The literature values are for dilute solutions; thus, the slight difference between our average and the literature value may result from concentration effects rather than ion exchange. The fact that the literature value for $D(\text{Rb}^+)/D(\text{Li}^+)$ is 1.5 indicates that the rubidium ion is more mobile than the lithium ion even in aqueous solution. Our slightly higher values probably imply that this difference in mobilities of these two ions is still greater at higher concentrations; our individual values of the ratio which are for comparable concentration agree well with each other. We conclude that no significant selectivity in diffusion exists for the Rb^+/Li^+ pair in any of the membranes tested.

The same conclusion can be made for the diffusion of the other ion pairs which we investigated. In table I, the values of $D(\text{Mg}^{++})/D(\text{Li}^+)$ average about 0.6 which is in agreement with the value for our "nonselective" porous membrane. The average is likewise in good agreement with the ratio of 0.7 obtained from the dialysis coefficients for the Mg^{++} and Li^+ ions through cellophane (ref. 6, p. 195). Again there was good agreement between the values for the various membranes. Except for the relatively large deviation for CaPA due to its lack of reproducibility, the greatest deviation from the average was 30 percent, that for the PAA membrane.

The average value of $D(\text{SO}_4^{=})/D(\text{Cl}^-)$ in table I is about 0.3; this is in fair agreement with the value for the purely porous membrane. Comparison with literature values is difficult because of the bisulfate ion which makes the effective diffusion coefficient of the sulfate species highly dependent on its concentration and ionic environment, particularly pH. Excluding values with low reproducibility, the greater deviation is about 30 percent. Thus, again no significant ion selectivity for diffusion of the ion pair is shown by the membranes tested.

The fact that the ratio of the D's for the various ion pairs is not unity (fig. 1) is attributable to the difference in the mobility of the individual ions in aqueous solution and not to properties of the membrane. However, earlier data implies that some of the membranes tested can exhibit ion selective diffusion behavior for larger, more complex ions. For example, the copper II ion forms a second phase with CaPA and thus the copper ion requires a long time period to diffuse through such a membrane (ref. 5). Therefore, the copper ion can be removed from simple ions by a diffusion process. Also, the diffusion of the complex zincate anion through PVA is extremely slow (ref. 3). The present research, however, indicates that we should not expect to find this ion selectivity for the diffusion of simple ions.

In contrast to our present findings, we have shown (May and Philipp, unpublished data) that cross-linked polyacrylic acid does exhibit selectivity toward Li^+ , Rb^+ , Mg^{++} , and other ions in actual ion exchange reactions.

Diffusion coefficients. - The effective diffusion coefficients for the various ions through the various membranes are listed in table II even though the values of D are not as meaningful as their ratios. For the molecular porous membranes (PVA, PAA, the copolymer, cellulose, and CaPA) the values of D are of the magnitude of $10^{-6} \text{ cm}^2/\text{sec}$, only slightly less than the diffusion coefficients of these ions through water (refs. 6, 9, and 10). The values of D through the microporous films (MgO-ppo , $\text{MgSiO}_3\text{-ppo}$, and porous ppo) are much lower. This arises from the tortuous paths of the pores as well as their limited number; the pores in these membranes exist apparently only at the grain boundaries of the ppo. The presence of filler fosters the formation of these pores or channels (ref. 8).

Experimental results for reused membranes generally were the same as for fresh ones. However, when the MgO-ppo films were reused, higher values of D resulted even though the ratio values were essentially the same. This is attributable to larger pore size resulting from dissolving out the MgO filler. Note that the intentionally leached films also exhibited higher values of D than did the MgO-ppo films.

A significant finding of this research is that the values of D for the ions through PAA are comparable with the values of respective ions through PVA, cellulose, and water, even though ion exchange occurs in the PAA and not in the other cases. The ion exchange occurs between the proton on the carboxylic acid group on the PAA and the diffusing cations: Rb^+ , Li^+ , and Mg^{++} . The changing composition of the PAA does not appear to inhibit the diffusion of these ions through the membranes. Thus Fick's law applies. Even the copper II ion which exchanges with the Ca^{++} ion as it diffuses through CaPA by a different mechanism (ref. 5) exhibits a value of D (about 3×10^{-7} cm^2/sec) comparable with the values of D for the simple ions through such membranes. Of course, another form of Fick's law is required to fit the experimental data.

CONCLUSIONS

The membranes tested showed no significant specificity for diffusion of simple ions. However, the calcium polyacrylate film exhibited ion exchange with the diffusing cations. In general, Fick's law appeared to be obeyed. The diffusion coefficients of the ions through the molecular porous membranes were found to be comparable with those of the respective ions through water. The coefficients for the microporous films were much less due to tortuosity and limited number of pores. The relatively rapid diffusion of simple ions through PAA and CaPA emphasized their potential use in ion exchange applications.

APPENDIX - METHOD OF CALCULATION

From Fick's law (ref. 11), we may write

$$F(i) = -D(i) \frac{dC(i)}{dX} = -D(i) \frac{C(i,l) - C(i,r)}{S} \quad (1)$$

where F is the flux; D is the apparent diffusion coefficient; dC/dX is the concentration gradient in the direction of flow; C is the concentration; S is the thickness of the membrane; the subscript i refers to ions of the i th type; and l and r refer to compartments (l) and (r), respectively. D is an involved function of the diffusion coefficients of all the ions present, their concentration gradients, and their ion charges (refs. 6 and 7). For the purpose of this report, D can be taken as an approximation to the true diffusion coefficient of the i th ion because we are for the most part interested only in the ratio of the D 's of two different ions.

Because the value of $C(i,l) - C(i,r)$ changes as our experiment proceeds, the average value should be used as given in the following equation.

$$F(i) = \frac{D(i)}{S} \left(\frac{M(i,l,b) + M(i,l,a)}{2 V(l)} - \frac{M(i,r,b) + M(i,r,a)}{2 V(r)} \right) \quad (2)$$

where M is the number of moles of species i in the compartment of volume, V ; b and a refer, respectively, to values before and after a diffusion period.

The flow of the i th ion can also be determined from the loss of the ion from compartment (l) or the gain in compartment (r).

$$F(i) = \frac{M(i,l,b) - M(i,l,a)}{T A} = \frac{M(i,r,a) - M(i,r,b)}{T A} \quad (3)$$

where T is the time interval and A is the diffusion area. In the procedure used,

$$M(i,r,b) = 0 \quad (4)$$

If we consider changes in the ion content of the membrane to be negligible, it follows that

$$M(i,l,b) = M(i,l,a) + M(i,r,a) \quad (5)$$

Combining equations (2) and (3) gives

$$D(i) = \frac{S V(l) M(i,r,a)/T A M(i,l,a)}{1 + M(i,r,a) (V(r)-V(l))/2 M(i,l,a) V(r)} \quad (6)$$

Each $M(i,r,a)$ is obtainable directly from chemical analysis; the $M(i,l,a)$, however, must be obtained by summing over all the subsequent values of $M(i,r,a)$ and the value of the final $M(i,l,a)$ because only the final value of $M(i,l,a)$ was obtainable directly from analysis. The ratio between two values of $D(i)$ can be obtained without knowing S , T , and A as can be seen from the following equation.

$$\frac{D(i)}{D(j)} = \frac{M(j,l,a)/M(j,r,a) + V(l)/2V(r) - 1/2}{M(i,l,a)/M(i,r,a) + V(l)/2V(r) - 1/2} \quad (7)$$

Thus, the value of $D(i)/D(j)$ is free of many errors that might be present in the individual value of $D(i)$. For example, equation (7) is free of errors due to irregularities in a membrane. If $V(r)$ is equal or nearly equal to $V(l)$ or if $M(i,r,a) \ll M(i,l,a)$, then equation (7) simplifies to

$$\frac{D(i)}{D(j)} = \frac{M(i,r,a) M(j,l,a)}{M(i,l,a) M(j,r,a)} \quad (8)$$

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TABLE I. - RATIO OF DIFFUSION COEFFICIENTS
FOR VARIOUS IONS AND MEMBRANES^a

Film	Wet thickness, mm	$\frac{D(\text{Rb}^+)}{D(\text{Li}^+)}$	$\frac{D(\text{Mg}^{++})}{D(\text{Li}^+)}$	$\frac{D(\text{SO}_4^{=})}{D(\text{Cl}^-)}$
PVA	0.38	1.9	0.6	0.2
PAA	.49	1.7	.8	.4
PVA-PAA Copolymer	.65	1.8	.7	.3
CaPA ^b	.40	1.4	.3	.2
Cellulose	.17	2.0	.7	.3
MgO-ppo	.08	1.9 ^c	.6	.2 ^e
MgSiO ₃ -ppo	.09	1.3 ^d	.5	.1 ^e
Leached ppo	.08	1.7 ^d	.6	.4 ^e
Averages		1.7	.6	.3

^aAverage reproducibility ± 5 percent.

^bReproducibility ± 10 percent; Ca⁺⁺ found
in diffusate.

^cMg⁺⁺ found in diffusate.

^dNo Mg⁺⁺ found in diffusate.

^eReproducibility poorer than ± 25 percent.

TABLE II. - APPARENT DIFFUSION COEFFICIENTS
THROUGH MEMBRANES

Film	$D \times 10^6 \text{ cm}^2, \text{ sec}^{-1}$				
	Li+	Rb+	Mg++	Cl-	SO ₄ =
PVA	2	3	1	2	0.4
PAA	4	5	4	5	3
PVA-PAA Copolymer	5	7	4	7	2
CaPA	.7	1	.2	4	.7
Cellulose	1	2	.7	2	.6
MgO-ppo	.03	.06	.02	.005	.001
MgSiO ₃ -ppo	.002	.002	.001	.004	.0006
Leached ppo	.4	.8	.2	.01	.006

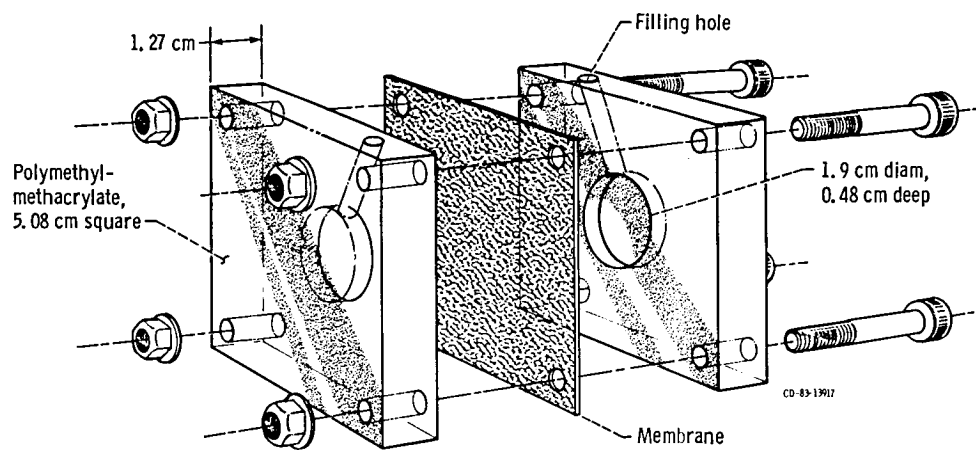


Figure 1. - Unassembled diffusion cell.

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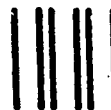
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